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Microwave Catalytic Conversion of SO_2 and NO_x over Cu/zeolite

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Abstract: Microwave catalytic technology is a promising technology for flue gas treatment. Cu/zeolite was used as catalyst for microwave catalytic desulfurization and denitrification and for microwave catalytic reduction of SO_2 and NO_x with ammonium bicarbonate (NH_4HCO_3) as a reducing agent. Microwave catalytic desulfurization and denitrification efficiency achieved 76.1 and 81.8% separately. The reaction efficiency of microwave catalytic reduction of SO_2 and NO_x could be up to 99.8 and 92.8% respectively. The physico-chemical properties of Cu/zeolite catalysts were characterized by X-ray diffraction analysis (XRD), Brunauer-Emmett-Teller measurements (BET), X-ray photoelectron spectrum analysis (XPS), scanning electron microscopy (SEM).The XPS results indicate that sulfide (SO_4^{2-}), element sulfur (S^0) and NH_4^+ species exist on the catalyst surface after the reaction. Microwave catalytic SO_2 and NO_x removal follows Langmuir — Hinshelwood(L-H) kinetics.

Key words: Simultaneous desulfurization & denitrification; Microwave catalytic technology; Cu/zeolite; Characterization

1. INTRODUCTION

Sulfur dioxide (SO_2) is generally accepted to be the most important precursor to acid rain[1]. Nitrogen oxides (NO_x) contribute a lot to photochemical smog, acid rain and ozone depletion[2]. Many technologies have been developed into remove of SO_2 and NO_x from flue gas, among which the catalytic technology is more effective. Catalytic reduction of SO_2 has been investigated using transition-metal oxide catalysts with C_2H_4 as a reducing agent[3]. Extensive research on selective catalytic reduction (SCR) of nitrogen oxides has been undertaken using ammonia[4] as reducing agent over various catalytic materials, such as CuO, Cu-loaded zeolites, H–ZSM-5, CeO_2- zeolites[5-8].

Simultaneous desulfurization and denitrification is a promising technology at high efficiency and low cost. Simultaneous SO_2 and NO_x removal could be achieved with high efficiency using CuO/Al_2O_3 , V_2O_5/AC[9-10]. Some research has been conducted in simultaneous desulfurization and denitrification by plasma technologies such as nonthermal plasma [11], electron beam and electrical discharge induced nonthermal plasmas [12], pulsed corona discharge generated by magnetic pulse compression modulator[13], a nonthermal plasma hybrid reactor using NiO/TiO_2,V_2O_5/TiO_2, and TiO_2 as catalysts[14]. Microwave was applied to a pyrolytic carbon such as activated carbon and char, enhancing reaction of sulfur dioxide (SO_2) and nitrogen oxides (NO) with carbon[15].

The reaction efficiency of microwave reduction of NO_x could be up to 98% when microwave energy was applied continuously[16]. The simultaneous treatment with the accelerated electronic beams and the microwaves could

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increase the removal efficiency of NO_x and SO_2, about 80% of NO_x and more than 95% of SO_2 were removed by precipitation with ammonia[18].

The objective of this work is to further improve the efficiency of desulfurization and denitrification simultaneously by microwave catalytic process using Cu/zeolite as catalyst. The study evaluates the role of microwave and catalyst, the influence of microwave power, empty bed residence time (EBRT) on desulfurization and denitrification simultaneously, and the mechanistic and kinetic analysis of microwave-induced catalytic SO_2 and NO_x removal were elicited. The study provides reliable data and key information for industrial applications.

2. EXPERIMENTAL

2.1 Catalyst Preparation

The Cu/zeolite was prepared by an incipient wetness impregnation using $Cu(NO_3)_2$ as the metal precursor. After impregnation in Ca-5A zeolite for 24 h in room temperature, the catalyst samples were dried in the drying oven at 32 ^{0}C for 36 h, and placed in the middle of muffle furnace, calcined at 550 ^{0}C for 120 min. After cooling to room temperature, the Cu/zeolite samples were taken out for further investigations.

2.2 Physico-chemical Characterization

The crystallinity of the prepared Cu/zeolite was identified using powder X-ray diffraction (XRD) on a D/Max-IIIA Rigaku X-ray diffractometer system equipped with a RINT 200 wide-angle goniometer using Ni-filtered Cu Kα radiation with a generator voltage and current of 35 kV and 25 mA, respectively. A scan speed of 5^0 (2θ min^{-1}) with a scan step of 0.002^0 (2θ) was applied during a continuous run in the 5-60^0 (2θ) range. Phase identification was carried out using the reference database (JCPDS-files) supplied with the equipment. The Brunauer Emmett Teller (BET) method, using a USA Micromeritics Corporation FlowSorb, was used to determine the total surface area of the prepared catalyst by N_2 adsorption/desorption at -195.8 ^{0}C. Surface element analysis was carried out by X-ray photoelectron spectrum analysis (XPS) using a Thermo ESCALAB 250 instrument with Al Kα radiation (hv= 1486.6 eV) at 150 W. The signal of adventitious carbon (a binding energy of 284.8 eV) has been used to calibrate the binding energy scale for X-ray photoelectron spectrum analysis (XPS) measurements. The Cu/zeolite was then examined by scanning electron microscopy (SEM) with a electron detector (Japan, JSM-6330F).

2.3 Microwave Catalytic Experiments

The microwave reactor consisted of a quartz tube (i.d. 10 and 250 mm long) with Cu/zeolite and ammonium bicarbonate (NH_4HCO_3) or Cu/zeolite only was set up to study removal of SO_2 and NO_x (NO, NO_2) from stimulated waste gas. A constant input microwave power of 164~331 W was used, and the microwave frequency was 2450 MHz.SO_2 and NO_x supplied from the gas cylinders, were first diluted with the compressed air, passed through an air mixture bottle and flowed upwards through the microwave reactor. The flow meter and the valve were used to monitor the gas flow through the reactor. SO_2 and NO_x (NO, NO_2) concentrations were analyzed by the device of S2000 flue gas, and gas flow rate was monitored by the rotameter and the mass flow controllers. In the process of the experiments, the simulated SO_2 and NO_x-containing flue gas were supplied to the microwave reactor, at a flow rate of 150~350 L.h^{-1} (EBRT, 0.153~0.358 s).

2.4 Analytical Methods

$FeAg/Al_2O_3$ catalyst surface element analysis was carried out by X-ray photoelectron spectrum analysis (XPS) using a Thermo ESCALAB 250 instrument with Al Kα radiation (hv= 1486.6 eV) at 150 W. The $FeAg/Al_2O_3$ was then examined by scanning electron microscopy (SEM) with an electron detector (Japan, JSM-6330F). The intermediate products were identified by analyzing them with a fourier transform infrared (FT-IR) spectrometer (model Vector 33, Bruker Co.).

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

The fine crystal of nanoscale Cu/zeolite is conglomerated and the surface of the Cu/zeolite sample is found to be porous (Fig.1). The BET surface area of Cu/zeolite is 107.89 m^2.g^{-1}; the total pore volume and average pore diameter of the corresponding sample are 0.1566 cm^3.g^{-1} and 5.8 nm, respectively.

The XRD pattern of Cu/zeolite catalyst used in this study is shown in Fig. 2. XRD pattern of Cu/zeolite catalyst shows two principal peaks at 2θ=35.7° and 38.74° which are characteristics of CuO; the principal peaks of Cu at 2θ= 7.22° do appear in XRD patterns of Cu/zeolite catalyst.

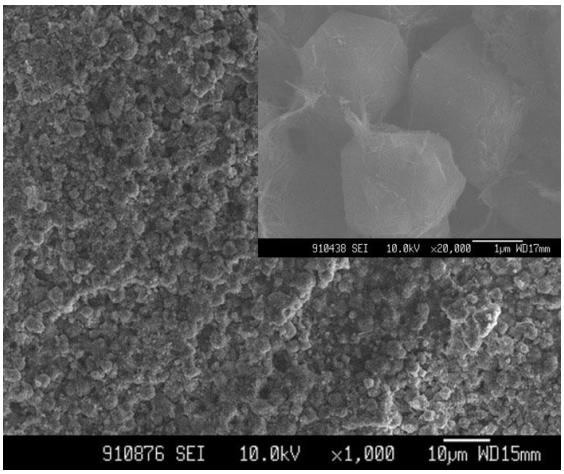

Fig. 1: SEM İmages of Cu/zeolite

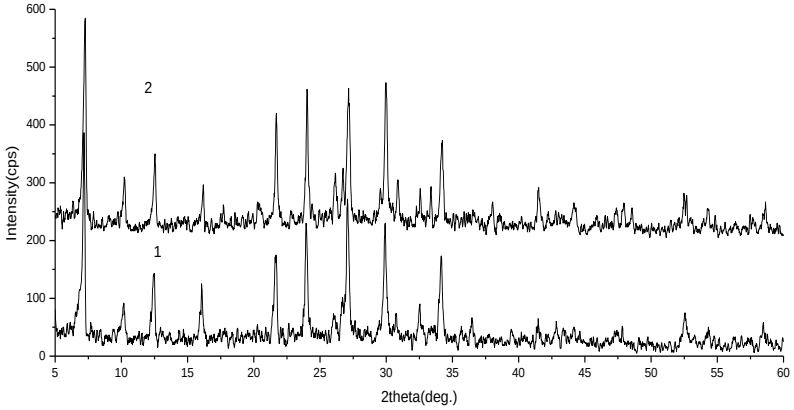

Fig. 2: XRD Patterns of Cu/zeolite (1) before and (2) after the Reaction

Photoelectron spectra of Cu2p, S2p, N1s levels for Cu/zeolite after the reaction are displayed in Fig. 3. High-resolution scan over Cu2p peaks showed that the binding energy of Cu2p was 933.6 eV, which indicated that Cu loaded on the catalyst existed as CuO. After the microwave catalytic reduction desulfurization and denitrification reaction, the S2p region showed a band centered at 168.8 eV, attributed to the sulfide (SO_4^{2-}) species, with a satellite peak at 164.1eV characteristic of sulfur (S^0); the N1s region showed a band centered at 399.6 eV, corresponding to NH_4^+ species.

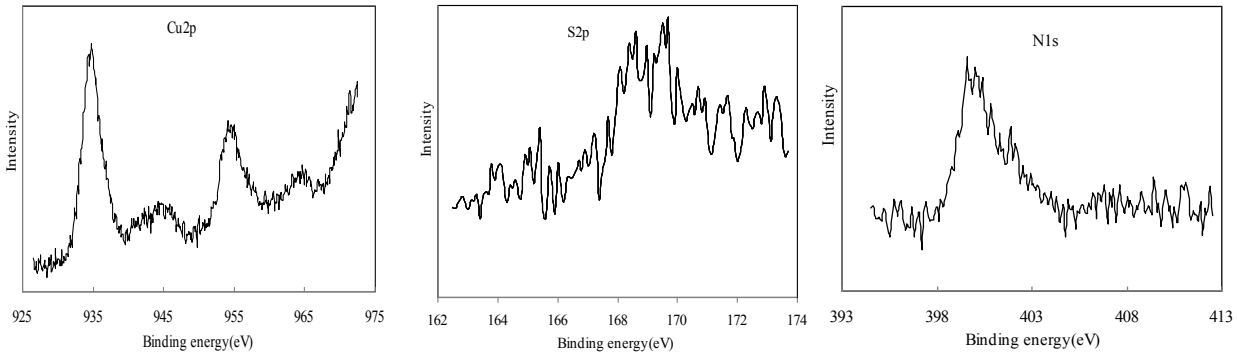

Fig. 3: XPS Spectra of the Core Levels for Cu/zeolite after the Reaction

3.2 Microwave Catalytic Desulfurization and Denitrification Performance

The influence of concentration of SO_2 and NO_x in inlet on desulfurization and denitrification are shown in Figs. 4 and 5, separately. The MWCu/zeolite and ABCu/zeolite profile are represented by Cu/zeolite under microwave and ammonium bicarbonate over Cu/zeolite separately. SO_2 removal efficiency decreases from 76.1 to 55.6% when the concentration of SO_2 is increased, while NO_x removal efficiency changes from 63 to 81.8% with increasing concentration of NO_x. This illustrates that Cu/zeolite catalyst has good performance of microwave catalytic desulfurization and dentrification under no reducing agent; and the microwave catalytic desulfurization and dentrification effect over Cu/zeolite is close to that of catalytic reduction of SO_2 and NO_x using ammonium bicarbonate as reducing agent and Cu/zeolite as catalyst.

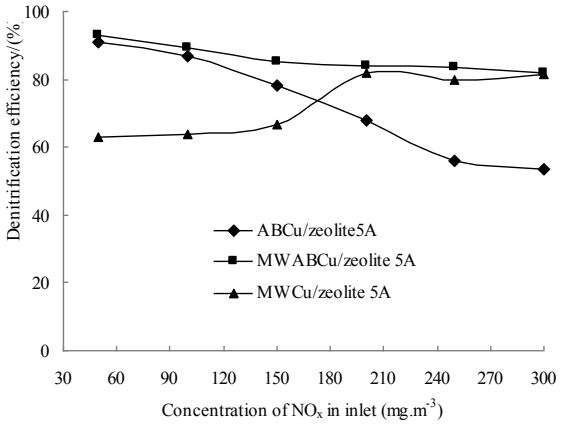

Fig. 4: Influence of Concentration of NO_x in İnlet on Denitrification under the Conditions with İnlet Concentration of SO_2 of 1000 mg.m-3 at 280 W of Microwave Power and EBRT of 0.358 s

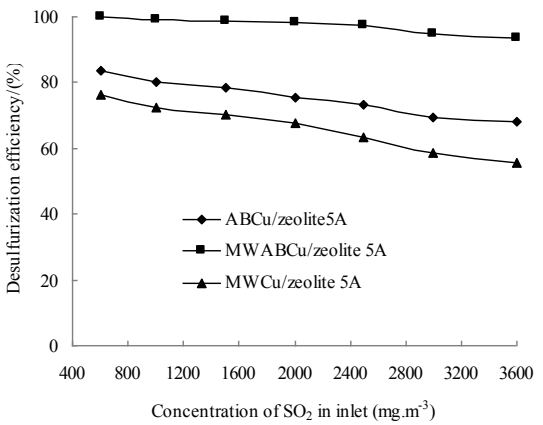

Fig. 5: Influence of Concentration of SO_2 in İnlet on Desulfurization under the Conditions with İnlet Concentration of NO_x of 250 mg.m-3at 280 W of Microwave Power and EBRT of 0.358 s

Thermal effects produced by microwave irradiation on mineral-supported catalyst seem to result from the formation of rapid superheating of the catalyst surface, which cause the high temperature hot spots[1]; microwave heating has been used to promote desulfurization[19]. However, the Cu/zeolite surface reaction temperature range of microwave catalytic desulfurization and dentrification was 73~125 ^{0}C, obviously lower than that of selective noncatalytic reduction (SNCR), 900-1100 ^{0}C. In our experiment, the high performance liquid chromatography (HPLC) was used to identify hydroxyl radicals, the results showed that the active OH free radicals existed in the microwave catalytic process (Wei et al., 2009). The free radicals with a high oxidation potential contribute to removal of SO_2 and NO_x; OH radicals not only can oxidize SO_2 leading to the formation of sulfate, but also can oxidize NO_x (NO, NO_2) resulting in the production of nitrate. This means that not microwave heating but microwave-catalytic -generated hydroxyl radicals gives rise to the observed oxidation of SO_2 and NO_x reactions. Basically microwave catalytic generated hydroxyl radicals play an important role in the oxidation of SO_2 to sulfate, and NO_x to nitrate, simultaneously.

$$O_2, H_2O \xrightarrow{microwave+Cu/zeolite} OH, O, HO_2$$
$$SO_2 + OH \rightarrow HSO_3, HSO_3 + OH \rightarrow HSO_4$$
$$NO + OH \rightarrow HNO_2, HNO_2 + OH \rightarrow HNO_3$$
$$NO_2 + OH \rightarrow HNO_3$$

3.3 Microwave Catalytic SO_2 and NO_x Reduction Performance

3.3.1 Microwave catalytic reduction of SO_2 and NO_x simultaneously

The MWABCu/zeolite profile is represented by ammonium bicarbonate and Cu/zeolite under microwave. As are shown in Figs. 4 and 5, microwave accentuates catalytic reduction of SO_2 and NO_x, and increases SO_2 removal efficiency from 16.2 to 25.6%, and NO_x removal efficiency from 1.9 to 28.5%. For comparison, in the presence of

microwave irradiation over Cu/zeolite, with/without ammonium bicarbonate (NH_4HCO_3) in flue gas treatment process, SO_2 removal efficiency increases from 23.7 to 37.9% and the denitrification efficiency increases from 0.5 to 29.8%.

The ammonium bicarbonate does not absorb microwave energy; microwave should not induce SO_2 and NO_x reduction without microwave absorbent such as Cu/zeolite. The Cu/zeolite catalyst does absorb microwave energy but requires the reducing agent such as ammonium bicarbonate. The use of both Cu/zeolite and ammonium bicarbonate combined with microwave energy would induce SO_2 and NO_x catalytic reduction reaction significantly. Thus, a major mechanism for microwave catalytic reduction of SO_2 and NO_x can be described as the microwave-induced catalytic reduction reaction between SO_2, NO_x, and ammonium bicarbonate, with Cu/zeolite being the catalyst and microwave absorbent. Microwave catalytic reduction of SO_2 and NO_x effect simultaneously are much higher than that of catalytic reduction or microwave catalytic desulfurization and dentrification, which are generally in the order: (MWABCu/zeolite) > (ABCu/zeolite) > (MWCu/zeolite)

XPS result confirms that sulfur (S^0) should have been formed as the reaction production from the reaction between SO_2 with ammonium bicarbonate or ammonia (NH_3). On the basis of the experiments as above, we assume that SO_2, NO_x from flue gas can react with ammonia (NH_3) decomposed by ammonium bicarbonate (NH_4HCO_3) to produce sulfur, nitrogen when NH_4HCO_3 and Cu/zeolite are used together under microwave, which is critical to microwave catalytic reduction desulfurization and denitrification simultaneously. The key reactions enhance the SO_2 and NO_x removal efficiency in the presence of ammonium bicarbonate (NH_4HCO_3) over Cu/zeolite under microwave.

A speculative mechanism can be based in these steps. 1) Zeolite concentrates the radiation, and helps to heat the surrounding. In consequence, the ammonium bicarbonate decomposes in NH_3, H_2O and CO_2. 2) This ammonia reacts with NO_x or SO_2 yielding N_2 H_2O and S. In this second step Cu centers can have an important role, because they are able to catalyze NO_x decomposition, and the SCR of NO_x with NH_3. But, CuO centers are not good catalyst for the decomposition of SO_2.

Therefore, a schematic of possible reactions is described below.

$$NH_4HCO_3 \rightarrow NH_3 + H_2O + CO_2$$
$$SO_2 + 8NH_3 + 2O_2 \rightarrow 4N_2 + 6H_2O + S$$
$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

3.3.2 The influence of microwave power and EBRT

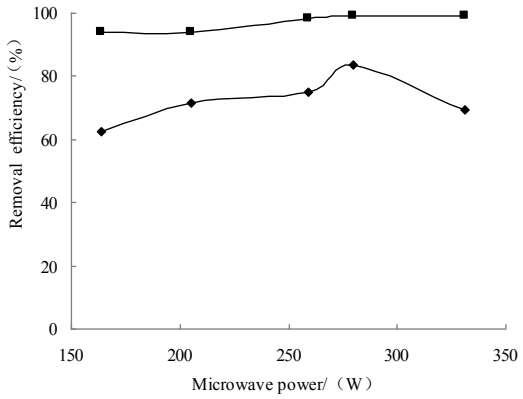

Fig. 6: Influence of Microwave Powers on Microwave Catalytic Reduction Desulfurization and Denitrification under the Conditions with İnlet Concentration of SO_2 of 1000 mg.m^{-3}, NO_x of 250 mg.m^{-3} at EBRT of 0.358 s

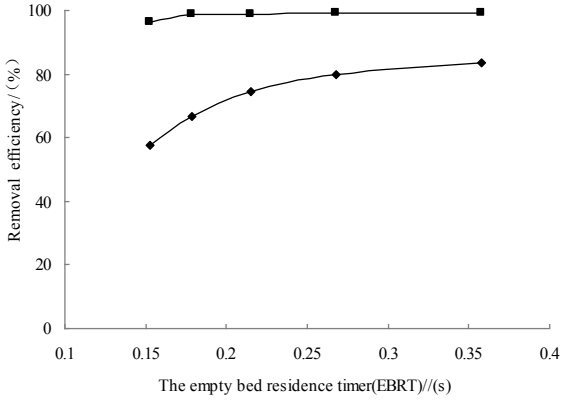

Fig. 7: Influence of EBRT on Microwave Catalytic Reduction Desulfurization and Denitrification under the Conditions with İnlet Concentration of SO_2 of 1000 mg.m^{-3} and NO_x of 250 mg.m^{-3} at 280 W of Microwave Power

Fig. 6 shows the influence of microwave power on simultaneous desulfurization and denitrification using ammonium bicarbonate as reducing agent and Cu/zeolite as catalyst. The conversion of desulfurization efficiency gradually increases from 93.8% with 164 W to 99.2% with 280 W, and then decreases to 99% with 331W; while the conversion of denitrification efficiency increases from 62.5% with 164 W to 83.6% with 280 W, decreases to 69.2% with 331W, showing excellent microwave catalytic reduction desulfurization and denitrification effect. The experimental results show that the optimum microwave power for microwave catalytic reduction desulfurization and denitrification simultaneously is supposed to be 280 W.

The influence of EBRT on microwave catalytic reduction desulfurization and denitrification simultaneously is presented in Fig.7. With EBRT increasing, SO_2 removal efficiency increases from 96.3 to 99.2%, whereas NO_x removal efficiency increases from 57.6 to 83.6%. Sulfur dioxide (SO_2) and nitrogen oxides (NO_x) are rapidly reduced at microwave power of 280 W, when ammonium bicarbonate and Cu/zeolite are added under microwave simultaneously. This indicates the longer EBRT is a benefit on the removal of SO_2 and NO_x, in the case where the EBRT is too short to reduce SO_2 and NO_x to sulfur and nitrogen before release. The type of Cu/zeolite catalyst and the length of the quartz tube with catalyst and reducing agent are the key elements.

3.4 Kinetic Evaluation

The Langmuir-Hinshelwood (L-H) rate expression has been widely used to describe the gas-solid phase reaction for heterogeneous catalysis[19]. Assuming that the SO_2 and NO_x mass transfer are not the limiting step, and that the effect of intermediate product is negligible, substrate SO_2 and NO_x are adsorption onto the surface of Cu/zeolite catalyst, then the reaction rate in a microwave reactor can be expressed as

$$r = -u\frac{dC}{dL} = \frac{kK}{1+KC} \tag{1}$$

where *k* and *K* are the L-H reaction rate constant and the L-H adsorption equilibrium constant, respectively; L is the length of the microwave reactor filled with NH_4HCO_3 over Cu/zeolite or Cu/zeolite only; and u is the gas velocity through the reactor. After rearrangement and integration of (1) the following linear expression can be obtained:

$$\frac{In\left(\frac{C_{in}}{C_{out}}\right)}{\left(C_{in}-C_{out}\right)} = \frac{kK\left(V/Q\right)}{\left(C_{in}-C_{out}\right)} - K \tag{2}$$

where C_{in} and C_{out} are the inlet and outlet concentrations of SO_2 and NO_x respectively, V is the volume of the microwave reactor (14.92 ml); and Q is the flow rate through the reactor (150 $L.h^{-1}$).

The values of L-H reaction rate constant *k* of the desulfurization is more than that of the denitrification (Table 1), the possible reason for this could be that concentrations of SO_2 are more than concentrations of NO_x under our experimental conditions. This demonstrates that the microwave reactor with NH_4HCO_3 over Cu/zeolite or Cu/zeolite has good desulfurization and denitrification effect, showing that desulfurization capacity is higher than that of denitrification. The values of L-H reaction rate constant *K* suggest that reaction occurs on the surface of Cu/zeolite catalyst through L-H mechanism and not in the gas phase. Hence, the microwave catalytic SO_2 and NO_x removal rate follows L-H kinetics.

Tab. 1: Kinetic Parameters for Microwave Catalytic SO_2 and NO_x Removal over Cu/ zeolite according to the L-H Rate Expression

Reaction	*k*(DS#)	*k*(DN*)	*K* (DS)	*K* (DN)
	$mg.m^{-3}.s^{-1}$	$mg.m^{-3}.s^{-1}$	$(mg.m^{-3})^{-1}$	$(mg.m^{-3})^{-1}$
MWCu/zeolite	11582.1	804.5	0.0003859	0.003
MWABCu/zeolite	96674.5	1361.9	0.0001277	0.007

#desulfurization, * denitrification

4. CONCLUSIONS

The present work provides a microwave catalytic technology as an efficient way of desulfurization and denitrification simultaneously. The microwave reactor with ammonium bicarbonate and Cu/zeolite or Cu/zeolite only can be used for desulfurization and denitrification simultaneously, and L-H kinetic model was successfully applied to describe this process on microwave catalytic SO_2 and NO_x removal. Microwave catalytic desulfurization and denitrification effect of the experiment using microwave reactor with Cu/zeolite only is close to that of catalytic reduction of SO_2 and NO_x using ammonium bicarbonate and Cu/zeolite together. Microwave catalytic reduction of SO_2 and NO_x simultaneously can be described as the microwave induced reduction catalyst reaction between SO_2, NO_x and ammonium bicarbonate with Cu/zeolite being the catalyst and the microwave absorbent.

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